Formation of a Linear Supramolecular Polymer by Self-Assembly of Two Homoditopic Monomers Based on the Bis(*m*-phenylene)-32-crown-10/Paraquat Recognition Motif

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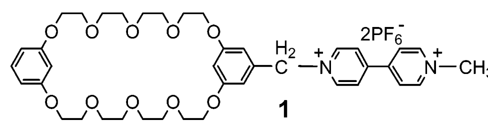
Received September 7, 2006; Revised Manuscript Received January 24, 2007

ABSTRACT: A homoditopic monomer containing two bis(*m*-phenylene)-32-crown-10 units and a complementary homoditopic monomer containing two paraquat moieties were designed and prepared. At high equimolar concentrations (>40 mM) they self-organize to form a linear supramolecular polymer in solution as confirmed by proton NMR spectroscopy, mass spectrometry, and viscosity studies.

Introduction

Inspired by nature, supramolecular chemistry is being widely studied with the aim of developing sophisticated self-assembled structures from small building blocks by molecular recognition, self-replication, and self-organization based on noncovalent interactions.[1] The combination of supramolecular chemistry and polymer science has led to the appearance of supramolecular polymers ("suprapolymers"), which are based on repeating units held together with directional and reversible noncovalent forces.[2] The introduction of noncovalent interactions enables some potential applications for suprapolymers. For example, the strong $\pi-\pi$ interactions within a column of discotic suprapolymers lead to their high electronic mobilities, a property that is essential in the development of plastic transistors and photovoltaics.[2b,3] The dynamic reversibility feature, resulting from the introduction of noncovalent forces, of suprapolymers allows slow release of active ingredients in pharmaceutical chemistry and medicine (controlled drug delivery), in agrochemistry, and in home and personal care.[2f] "Dynamers"[2f] present environmental and biological degradability, a feature of high potential interest in areas as different as biomedical applications[4] and waste management.[2f] Because of their simplicity in preparation and promising new properties, linear suprapolymers have attracted strong attention.[2,5−11] Some recognition motifs used in the construction of linear suprapolymers are multiple hydrogen bonding,[5] crown ether/organic salt host−guest binding,[6,7] cyclodextrin-based hydrophilic/hydrophobic interactions,[8] CO_2 linking with calixarene capsules via hydrogen bonding,[9] and nucleobase-pair interactions.[10] Though linear suprapolymers have been widely studied, linear suprapolymers fabricated from homoditopic monomers based on host−guest and pseudorotaxane[12] recognition motifs are still rare, while condensation polymerization of two difunctional monomers is commonly used in the preparation of traditional linear polymers. Here we report more of our studies directed toward the formation of linear suprapolymers from self-assembly of two complementary homoditopic monomers based on the well-studied bis(*m*-phenylene)-32-crown-10 (BMP32C10)/paraquat (PQ) recognition motif.[13]

Among our efforts with the BMP32C10/PQ systems was an early attempt to utilize it in preparation of suprapolymers via a heteroditopic (AB) monomer, **1**. This system in high concentration solutions displayed high viscosity (η_{red} > 0.25 dL/g) that enabled fibers to be drawn; however, the fibers were brittle, and mass spectrometry was able to detect oligomers only up to the tetramer.[7a] In this case NMR studies revealed the complexation−decomplexation processes to be rapid relative to the NMR time scale. At the same time we began to explore the use of homoditopic (AA/BB) monomers based on this molecular recognition motif. This required bis(crown ether) and bis(paraquat) monomers.



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Results

A. Design and Synthesis of Monomers. We chose to prepare the homoditopic host **2** by the reaction of 5-hydroxymethylene-1,3-phenylene-1′,3′-phenylene-32-crown-10[14] and terephthaloyl chloride. The homoditopic guest **3** was prepared by the reaction between *p*-xylylene-*N*,*N*′-bis(4,4′-bipyridinium) bis(hexafluorophosphate)[15] and 2-iodoethanol followed by anion exchange. These monomers were fully characterized.

Interaction of the host and guest moieties in these monomers is expected to produce cyclic and linear species (Scheme 1), the ratio of which depends on a number of factors, including the concentrations and the nature of the linking groups. The average degree of polymerization, *n*, has been shown to be related to the equilibrium constant K_a and the initial monomer concentration.[7c] Assuming that no cyclics form[17]

$$n = 1/(1 - p) = 2K_a[H]_0/\{(1 + 4K_a[H]_0)^{1/2} - 1\} \quad (1)$$

$$\text{if } 4K_a[H]_0 \gg 1,\ n = 2K_a[H]_0/\{(4K_a[H]_0)^{1/2} - 1\} \quad \text{and}$$
$$\text{if } (4K_a[H]_0)^{1/2} \gg 1,\ n = (K_a[H]_0)^{1/2} \quad (2)$$

In this system *p* is the fraction of host and guest moieties bound to each other in equimolar solutions and $[H]_0 = 2[\mathbf{2}]_0$. This

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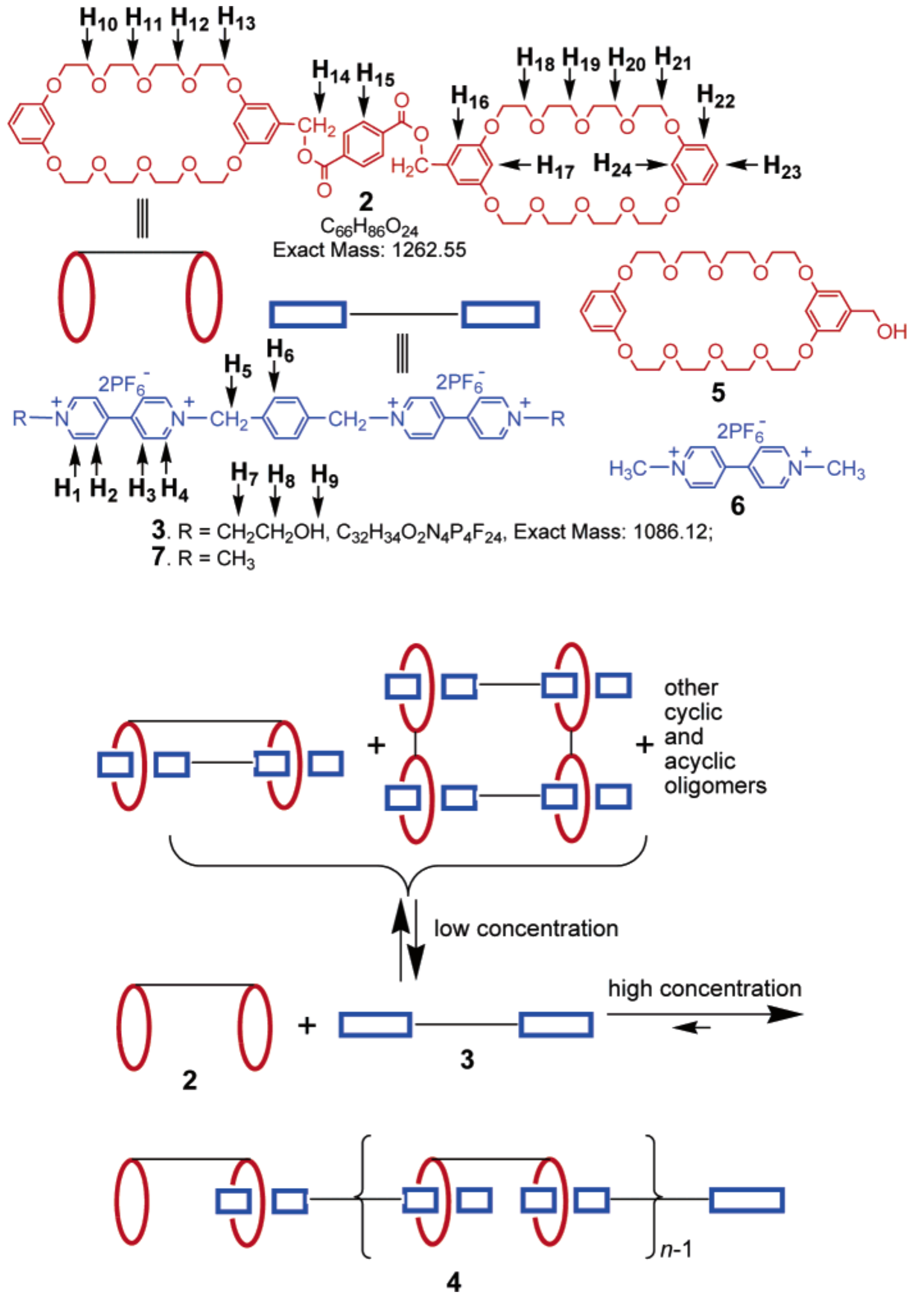
10.1021/ma062080i CCC: $37.00
Published on Web 04/13/2007

Scheme 1. Schematic Illustration of the Formation of Cyclic Oligomers at Low Concentration and Linear Suprapolymer 4 at High Concentration Based on the Self-Assembly of the Complementary Homoditopic Host 2 and Homoditopic Guest 3[a]



[a] Pseudorotaxane structures are indicated,[16] but the interaction may produce "taco" complexes, as several crystal structures show.[13b−d,h,j,k]

treatment also assumes that the K_a value does not vary with the size of the self-assembly, i.e., is isodesmic.[18] Therefore, degrees of polymerization calculated in this way represent maximum values that in practice will be reduced by formation of cyclics and possibly by reduction in the association constant as the suprapolymer grows ("attenuation"[18]).

B. Model Systems. To estimate the K_a value for interaction of **2** with **3** we refer to a model system. Interaction of dimethylparaquat (**6**) with BMP32C10 alcohol **5** proceeded with $K_a = [\mathbf{5}\cdot\mathbf{6}]/[\mathbf{5}][\mathbf{6}] = 824 \pm 82\ M^{-1}$ in acetone.[13j]

C. Proton NMR Characterization. Upon mixing **2** and **3** in acetone, a dark yellow-orange color developed immediately, indicating complex formation involving charge transfer. As with other examples of crown ether−paraquat complexes studied,[7a,13] the proton NMR spectrum revealed upfield shifts for all the protons except the terephthaloyl aromatic proton and the γ-OCH_2 (ethyleneoxy) protons, the latter undergoing a downfield shift. As expected, the proton NMR spectra of equimolar solutions of **2** and **3** (Figure 1) are concentration-dependent, reflecting the involvement of fast-exchanging noncovalent interactions in solution. When the initial concentrations were increased, the chemical shift change of H_1 on bis(paraquat) **3**, Δ, increased very sharply at first then very slowly above 10.0 mM (Figure 2). This demonstrated that the percentage of complexed paraquat moieties increased with increasing initial concentrations of **2** and **3**, suggesting the formation of linear suprapolymer **4**. At concentrations above 60 mM the solutions were too viscous to obtain good spectra.

We have demonstrated that the complexes of bis(*m*-phenylene)-32-crown-10/paraquat systems are ion paired as are the paraquat salts.[13f] Thus, values of the fraction *p* of complexed paraquat moieties at different initial concentrations of **2** can be estimated if Δ_0, the chemical shift change associated with fully complexed paraquat units, is known.[19] This Δ_0 value was

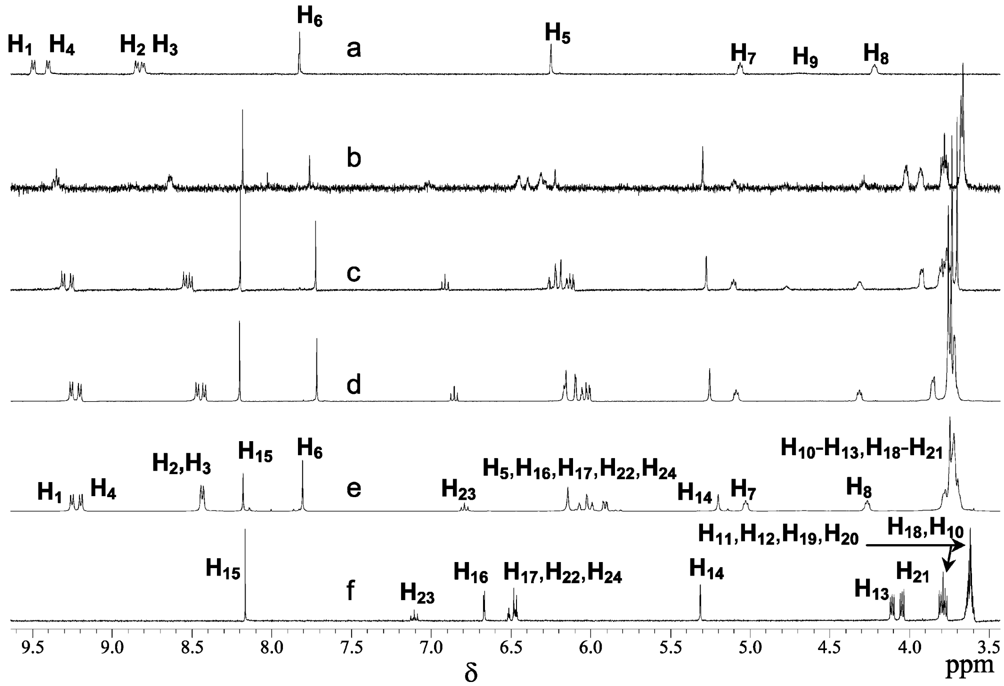


Figure 1. Partial proton NMR spectra (400 MHz, acetone-d_6, RT) of **3** (a); mixtures of **2** and **3** (molar ratio 1:1) at different concentrations: (b) 0.130, (c) 1.00, (d) 10.0, and (e) 60.3 mM; (f) **2**.

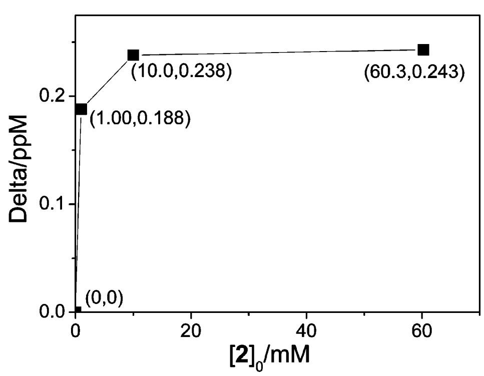


Figure 2. Relationship between Δ, chemical shift change of H_1 on homoditopic guest **3**, and [**2**]$_0$, the initial concentration of homoditopic host **2**.

Table 1. Values of *p* and Calculated Values of *n* in Equimolar Solutions of 2 and 3

[**2**]$_0$ = [**3**]$_0$ (mM)	p^a	max n^b (exp)	max n (theory)^c	max n (theory)^d
0.130	0.236 ± 0.12	1.31 ± 0.2	1.85 ± 0.12	1.18 ± 0.02
1.00	0.752 ± 0.12	4.03 ± 0.21	4.03 ± 0.35	1.88 ± 0.06
10.0	0.952 ± 0.24	20.8 ± 7.0	11.6 ± 1.1	4.59 ± 0.20
60.3	0.972 ± 0.24	35.7 ± 26.5	27.6 ± 2.7	10.5 ± 0.5

^{a} Calculated from $p = \Delta/\Delta_0$;[19] error bars reflect a potential error of 0.003 ppm in Δ. ^{b} Calculated from $n = 1/(1 - p)$;[22] this assumes that all complexed species are linear. ^{c} Calculated using eq 1: $K_a = (6.10 \pm 1.22) \times 10^3$ M^{-1} and [H] = 2[**2**]$_0$; this also assumes that all complexed species are linear. ^{d} Calculated using eq 1: $K_a = 824 \pm 82$ M^{-1} (K_a for **5·6**) and [H] = 2[**2**]$_0$; this also assumes that all complexed species are linear.

estimated to be 0.250 ppm using an acetone-d_6 solution with 0.200 mM of **3** and 40.0 mM of **5**. Using this value, the fraction p of complexed moieties in the various solutions was estimated (Table 1). From the data point at 1.00 mM we estimated $K_a = p/(1 - p)([\mathbf{2}]_0 - p[\mathbf{3}]_0) = 6.10 \times 10^3$ M^{-1} (with an error of ∼±20% perhaps); this value is 7.5-fold higher than the value for the model system **5·6** discussed above. This is interesting in view of the fact that we have observed[20] cooperative complexation[21] of bisparaquat **7** with a monotopic BMP32C10-based three-bridge cryptand host, meaning that complexation of the second paraquat unit is more favorable thermodynamically after the first paraquat unit has been bound. It appears that complexation of bisparaquat **3** with biscrown **2** is also cooperative; this would enhance the overall possibility of forming the target suprapolymer **4**. However, see the discussion below for an alternative and more likely explanation.

Using the Carothers equation[22] and assuming that only linear species were present, the fractional complexation values were used to calculate maximum possible degrees of polymerization (Table 1). When the concentrations are low, the calculated sizes of the aggregrates are small. When the concentrations of **2** and **3** increase, although the precision of p and hence n decreases, the calculated size of aggregrates increases to truly large values, suggesting that linear supramolecular polymer **4** is formed. For example, at [**2**]$_0$ = [**3**]$_0$ = 60.3 mM, a degree of polymerization of 35.7 would correspond to a polymer with molar mass 83.8 kDa.

The experimentally derived values of n calculated from p are more consistent with the theoretical values calculated using the K_a deduced for **2·3** than with those calculated using the K_a of **5·6**; again this seems to point to some degree of cooperativity[21] for **2·3**, which could be the result of some conformational change in either the host or the guest upon complexation of one of its binding sites.[21] However, see the discussion below.

D. Mass Spectrometry. The MALDI-TOF mass spectrum (Figure 3) provided support for the formation of oligomeric species. The base peak (100%) at m/z 1102 was assigned as $[\mathbf{2{\cdot}3} - \mathbf{F1} - \mathbf{F2} - PF_6]^+$. Two peaks were found that result from **3·2·3**: m/z 2551 $[\mathbf{3{\cdot}2{\cdot}3} - \mathbf{F3} - 2PF_6]^+$ (55%) and 2590 $[\mathbf{3{\cdot}2{\cdot}3} - \mathbf{F3} - 2PF_6 + H + K]^+$ (13%). A peak at m/z 3811 corresponds to a fragment of **2·3·2·3**: $[\mathbf{2{\cdot}3{\cdot}2{\cdot}3} - \mathbf{F3} - 2PF_6 - H]^+$ (9%). A peak was observed for **3·2·3·2·3** at m/z 5079: $[\mathbf{3{\cdot}2{\cdot}3{\cdot}2{\cdot}3} - \mathbf{F4} - HPF_6 + Na]^+$ (3%). Since the MALDI-TOF spectra depend on the ability of the molecule to be volatilized under the experimental conditions, the possibility of the presence of still higher units in the ionic polymer cannot be ruled out. Another likely reason that only small oligomers were

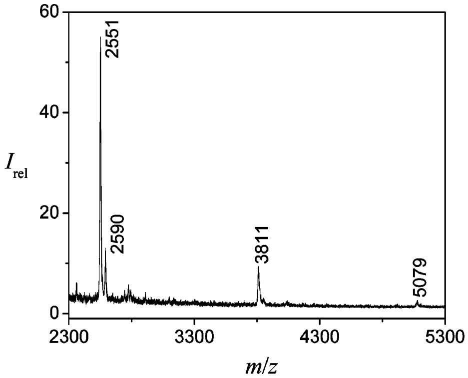
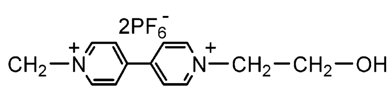
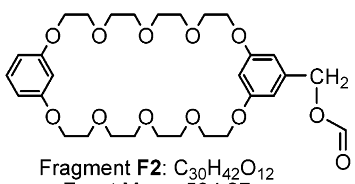


Figure 3. Partial MALDI-TOF mass spectrum of linear suprapolymer **4** formed from **2** and **3**. The spectrum was measured in the positive-ion mode using 2,5-dihydroxbenzoic acid as the matrix and acetone as the solvent.

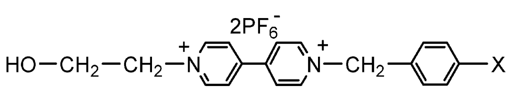
observed is that the degree of polymerization *n* for the supramolecular polymer formed from **2** and **3** is concentration-dependent (eq 1), and the sample solution used for MALDI-TOF mass spectrometry was dilute, so only small aggregrates were present.



Fragment **F1**: $C_{13}H_{15}N_2OP_2F_{12}$
Exact Mass: 505.05



Fragment **F2**: $C_{30}H_{42}O_{12}$
Exact Mass: 594.27



Fragment **F3**: X = CH_2
$C_{20}H_{21}N_2OP_2F_{12}$
Exact Mass: 595.09

Fragment **F4**: X = nil
$C_{19}H_{19}N_2OP_2F_{12}$
Exact Mass: 581.08

E. Viscosity Study. Viscous flow is characteristic of polymer solutions. Therefore, we turned to viscometry for direct physical evidence of the formation of linear suprapolymer **4**. Specific viscosities of acetone solutions of equimolar mixtures of **2** and **3** were measured as a function of concentration. A log−log plot of the resultant data is shown in Figure 4. In the low concentration range, the curve has a slope of 1.02, demonstrating a linear relationship between specific viscosity and concentration, which is characteristic for noninteracting assemblies of constant size;[23] these results indicate the presence of cyclic unimer in dilute solutions, as observed in other systems.[5,7b,c] With increasing concentration, a sharp rise in the viscosity is observed (slope = 2.08). This stronger concentration dependence indicates the formation of suprapolymers of increasing size. From Figure 4, a critical monomer concentration, $[M]_{crit}$, above which the concentration of cyclics no longer increases and linear species are produced exclusively,[24,25] was determined from the onset of the steeper portion, yielding a value of 80 mM for the initial concentration of crown units, corresponding to 40 mM for the initial concentrations of **2** and **3**. This value is comparable to values of $[M]_{crit}$ reported for ditopic ureidopyrimidone systems: 10−200 mM.[5] However, the lower slope above $[M]_{crit}$

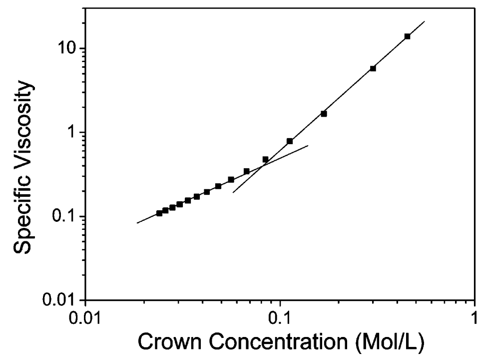


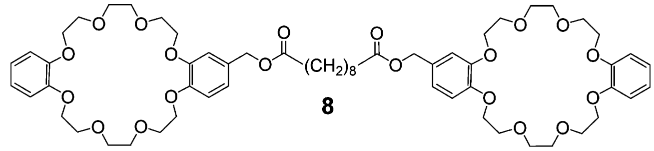
Figure 4. Specific viscosity of acetone solutions of equimolar mixtures of **2** and **3** as a function of concentration.

compared to those of the latter systems (slopes of 3−6)[5] and the theroeteically predicted value of 3.5−3.7[26] are consistent with the lower association constant of the present system and the fact that these systems are ionic and the solvent is organic. Indeed, the present slope is comparable to that observed with homoditopic systems comprised of bis(dibenzo-24-crown-8) **8** and bis(dibenzylammonium) salts **9**; in those systems, depending on the length of the aliphatic spacer in the diammonium guest species, slopes of 1.48, 2.83, and 2.64 were observed.[7c] Those systems possessed association constants similar to that of the present homoditopic system.[27]

At the highest measured crown concentration, 0.45 M, the reduced viscosity in the equimolar solution of **2** and **3** was 0.26 dL/g. In order to reach this reduced viscosity value, the molar concentration had to be 1.4 M for solutions of heteroditopic monomer **1**. This indicates that the interaction between crown ether moiety and paraquat moiety is stronger for the system based on **2** and **3** than for the system based on **1**. There are at least three possible reasons. First, the crown ether moiety and paraquat moiety are directly connected to each other in **1** so the electron-donating effect of the crown ether moiety can decrease the binding ability of the paraquat moiety to the crown ether moiety and the electron-withdrawing effect of the paraquat moiety can decrease the binding ability of the crown ether moiety to the paraquat moiety. Second, monomer **1** is quite rigid, and this constrains the number of conformations of the complexes, resulting in a great deal of entropic cost. Third, the above-mentioned possible cooperative effect for the complexation between bisparaquat **3** and biscrown **2** may contribute.

Discussion

It is clear from the viscosity results that the NMR data in Table 1 lead to overestimation of the degrees of polymerization in this system. Although high degrees of complexation are achieved at relatively low concentrations, cyclic species dominate up to the $[M]_{crit}$ at $[\mathbf{2}]_0 = [\mathbf{3}]_0 = 40$ mM. Only above that point does the fraction of linear species increase to a sufficient level to produce polymeric structures **4**. This is similar to the situation observed with the bis(dibenzo-24-crown-8)/bis(dibenzylammonium) system **8**/**9**; in that case slow exchange made



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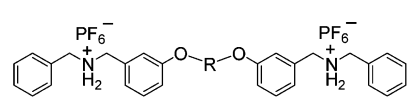
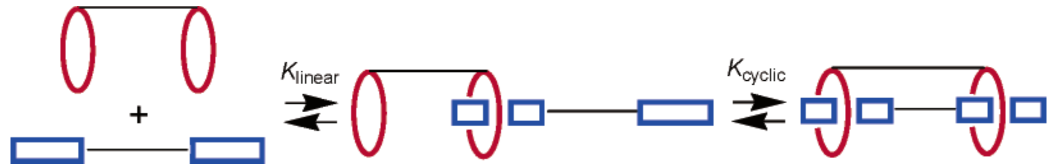


9 a. R = $(CH_2)_4$; b. R = $(CH_2)_{10}$; c. R = $(CH_2)_{22}$

Scheme 2. Formation of Linear and Cyclic Unimers by Interaction of Complementary Homoditopic Building Blocks



possible the detection of the cyclic species distinct from the linear species.[7b,c] The proportion of cyclic unimer vs linear unimer (Scheme 2) reflects the intramolecular complexation process; this was shown to depend on the length of the flexible aliphatic linkers in the diammonium salts **9** and the bis(crown ether) **8**: for spacers with combined lengths of 20 atoms (**8**/**9a**), 26 atoms (**8**/**9b**), and 38 atoms (**8**/**9c**) the K_{cyclic} (= [cyclic unimer]/[linear unimer]) values were 2.5, 1.7, and 0.62,[7c] corresponding to effective molarities (EM, the concentration above which formation of larger linear species is favored)[28] of 0.96, 0.23, and 0.060 mM for the unimers, respectively. K_{cyclic} decreases with increasing degree of polymerization to the 5/2 power, i.e., $n^{5/2}$,[24] meaning that in the case of large rings such as these the cyclic unimer predominates over larger cyclics. **8**/**9a**, **8**/**9b**, and **8**/**9c** yielded fractions of cyclics of 78/17%, 66/12%, and 28/0% for 10 mM/500 mM equimolar solutions in which p = 0.91/0.87, 0.84/0.92, and 0.66/0.95, respectively.[7c] These results agree with similar studies of other systems[5] and conform to the elegant theory developed by Ercolani et al.[25] In the present system (**2**/**3**) the relatively short linkers (a total of 16 atoms) and their rigidity favor cyclization (larger K_{cyclic}, higher EM) (as demonstrated by the results of Kricheldorf et al. on formation of covalent cyclic polymers),[29] and the extent of cyclic formation is undoubtedly relatively higher than in the former (**8**/**9**) system. This explains the higher apparent K_a deduced from the results presented in Figure 2; the fractional complexation is increased substantially by the highly favorable intramolecular formation of the cyclic unimer (Scheme 2); indeed, the viscosity results demonstrate that linear oligomers are not present in significant amounts at concentrations <40 mM. Comparison of the K_a deduced from Figure 2 (6.10×10^3 M^{-1}) with that of the model system **5/6** (824 M^{-1}) suggests that in the present case K_{cyclic} is 7.5; this appears reasonable in view of the prior results with **8**/**9** and the arguments above. It is estimated using eq 1 and K_a = 824 M^{-1} (the value for the model system) that at the highest concentration (0.5 M) $n = 20.7$, assuming that the concentration of cyclics is negligible. Although this degree of polymerization is far below the nominal value of 100 normally cited as a minimum for step-growth polymers, it corresponds to a respectable number-average molecular weight of 48.6 kDa.

It is, therefore, clear that in order to self-assemble suprapolymers of the pseudorotaxane type with degrees of polymerization ≥100, the building blocks must possess high association constants, good solubility (eqs 1 and 2), and reduced propensity for formation of cyclics.[30] Our recent success with cryptands as designed hosts for paraquats, with association constants up to 5×10^6 M^{-1},[31] and the results of our prior efforts pave the way for construction of appropriate monomers to achieve this goal.

Conclusions

In summary, we designed and synthesized a homoditopic monomer containing two bis(m-phenylene)-32-crown-10 units and a complementary homoditopic monomer containing two paraquat units. They can self-organize to form a linear supramolecular polymer in concentrated solution. The present results provide proof of principle for a method of construction of reversible (pseudorotaxane[12]) and potentially permanent (rotaxane,[12] by attachment of appropriate blocking groups on the paraquat units) mechanically linked linear suprapolymer systems. Our present efforts are aimed at these goals.

Experimental Section

Proton NMR Characterization, Viscosity Measurements, and MALDI-TOF Spectrometry. All solutions were prepared as follows. Precisely weighed amounts of dried hosts and guests were added into separate screw cap vials. The solvent was added with to-deliver volumetric pipets. Then specific volumes of each fresh solution were mixed to yield the desired concentrations. For example, in order to make a solution, 10.0 mM **2**/10.0 mM **3**, a 20.0 mM solution of **2**, and a 20.0 mM solution of **3** were made first by adding 2.00 mL of acetone-d_6 with a 2.00 mL to-deliver pipet into a screw cap vial containing 50.5 mg (0.0400 mmol) of **2** and another vial containing 43.4 mg (0.0400 mmol) of **3**. Then 0.300 mL of each of these two solutions was added with a 0.300 mL to-deliver pipet to a vial to make the target solution with 10.0 mM **2** and 10.0 mM **3**. ^{1}H NMR data were collected on an INOVA 400 proton NMR instrument. The solvent used for all solutions was acetone-d_6. Viscosities were measured with acetone as the solvent at room temperature in a Cannon-Ubbelohde semi-microdilution viscometer with 200 cP inner diameter capillary. The mixture of **2** and **3** (molar ratio 1:1) was submitted for MALDI-TOF as a solid after drying in vacuum. The sample was dissolved in acetone and mixed with the 2,5-dihydroxbenzoic acid matrix in acetone. The spectrum was recorded in the positive mode on a PerSeptive Voyager RP-DE MALDI-TOF mass spectrometer.

Bis(5-methylene-1,3-phenylene-1′,3′-phenylene-32-crown-10) Terephthalate (2). Terephthaloyl chloride (1.01 g, 4.93 mmol) was added to a solution of 5-hydroxymethylene-1,3-phenylene-1′,3′-phenylene-32-crown-10[14] (**5**, 5.64 g, 9.96 mmol) in anhydrous THF (125 mL) containing pyridine (0.900 mL, 11.1 mmol), and the mixture was refluxed for 48 h. After cooling, the precipitated pyridinium hydrochloride salt was filtered, and the organic layer was washed with water and 10% HCl (25 mL) solution. The organic layer was dried over anhydrous sodium sulfate and evaporated to dryness. The crude product was purified by silica gel column chromatography with ethyl acetate as the eluent. Evaporation of the solvent gave **2** (5.30 g, 85%) as an oil. Recrystallization from 2:8 dichloromethane/hexane gave a white solid; mp 75.7−77.9 °C. TGA: 5% weight loss at 375 °C in air (10 °C/min). IR (neat): 2924 (−CH), 1722 (C═O), 1596, 1489, 1456 (C═C), 1264 (C−C(═O)−C), and 1124 (C−O−C). ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C) δ (ppm): 8.11 (4H, s), 7.11 (2H, m), 6.57 (4H, d, J = 2.2 Hz), 6.48 (8H, m), 5.26 (4H, s), 4.07 (16H, m), 3.83 (16H, m), 3.69 (32H, m). ^{13}C NMR $CDCl_3$ δ (ppm): 66.94, 67.45, 67.58, 69.59, 69.64, 70.83, 70.85, 101.16, 101.612, 106.91, 107.03, 129.67, 129.74, 133.88, 137.68, 159.92, 160.08, 165.49 (18 peaks, theory 19). LR FAB MS (NBA/PEG) m/z (rel int): 1260.7 $(M)^+$ and 1097.5 ($M^+ - C_{10}H_{11}O_2$). HR FAB MS (NBA/PEG) m/z calcd for $[M]^+$ $C_{66}H_{86}O_{24}$ 1262.5509; found 1262.5461; error 3.8 ppm. Anal. Calcd for $C_{66}H_{86}O_{24}$: C, 62.73; H, 6.86. Found: C, 62.65; H, 6.86.

***p*-Xylylene-*N*,*N*′-bis[*N*′′,*N*′′′-bis(*β*-hydroxyethyl)-4,4′-bipyridinium] Tetrakis(hexafluorophosphate) (3).** To 2-iodoethanol (58.0 g, 337 mmol) in a 250 mL one-necked flask, p-xylylene-N,N'-bis(4,4′-bipyridinium) bis(hexafluorophosphate)[15] (2.54 g, 3.60 mmol) was added. The flask was immersed in an oil bath at 80 °C and magnetically stirred under nitrogen for 36 h. The unreacted 2-iodoethanol was recovered by filtration. The filtrate was dissolved in minimum deionized water. Excess NH_4PF_6 was added into this solution until no more precipitate formed. The resultant mixture was filtered to afford a white solid, which was recrystallized in water three times to afford **2** as a while solid, 3.29 g (84%): mp 202−203 °C. ^{1}H NMR (400 MHz, acetone-d_6, 22 °C) δ (ppm): 9.49 (d, J = 7.0 Hz, 4H), 9.40 (d, J = 7.0 Hz, 4H), 8.84 (d, J = 7.0 Hz, 4H), 8.80 (d, J = 7.0 Hz, 4H), 7.82 (s, 4H), 6.24 (s, 4H), 5.10 (t, J = 5.0 Hz, 4H), 4.70 (t, J = 5.0 Hz, 2H), 4.22 (q, J = 4.6 Hz, 4H). Anal. Calcd for $C_{32}H_{34}N_4O_2P_4F_{24}$: C, 35.37; H, 3.15; N, 5.16. Found: C, 35.62, 35.58; H, 3.52, 3.52; N, 5.14, 5.21.

Acknowledgment. This work was supported by the National Science Foundation (DMR0097126) and the Petroleum Research Fund (40223-AC7). F. Huang thanks the National Natural Science Foundation of China (20604020) and Zhejiang Province (2006R10003) for financial support.

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MA062080I